Recovery of wastes by pyrolysis: effect of experimental conditions

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Abstract

This work aimed to study the recovery of three types of waste by the process of pyrolysis: biomass, plastics and used tyres. The effects of experimental conditions in products yield and composition were studied. The increase of reaction time increased alkane content both in gas phase from 53% to 70% v/v and in liquid fraction from 48% to 60% w/w. The rise of reaction temperature led to a decrease of liquid yield (from 82% to 73% w/w), which was followed by the increase of solids and gases. The increase of reaction temperature also allowed the increase of the alkane content in gas phase from 39% to 70% v/v. The increase of initial pressure did not lead to appreciable variations in product yields or composition. The parameter that most affected products yield and composition was plastics content on the wastes initial mixture. The enhancement of this parameter increased liquids yield from 33% to 92% w/w, at the expenses of solids and gases contents and also decreased aromatics contents from 52% to 28% w/w.

Keywords: Pyrolysis, plastics, biomass, tyres, waste.

1 Introduction

Plastic, biomass and tyres wastes are three kinds of residues that presently pose difficulties when addressing their final post-use destination. The main alternatives employed today are incineration and landfill deposition. However, these are far from optimal treatment options, because they can raise environmental issues, like toxic and greenhouse gas emissions, leachates, etc, besides wasting their organic content that could be otherwise valuable in several applications. One of the promising ways of taking profit of the energetic and organic value of these wastes is by pyrolysis.

Several authors have studied the pyrolysis of these wastes in order to demonstrate its potentialities as a recycling alternative, e.g. Kaminsky *et al* (1997), Scott *et al* (1990), Conesa *et al* (1997), Williams *et al* (1997), Lee *et al* (2007), Fortuna *et al* (1997), Pinto *et al* (2001), Miranda *et al* (2004), Bridgwater (2002), Demirbas *et al* (2002), Karaca (2006), Tang *et al* (2005), Onay *et al* (2003), Hosoya *et al* (2007), Demirbas (2002).

In the present work three types of waste: plastics, tyres and biomass were pyrolyzed with the aim of studying the experimental conditions that maximize liquid yields. The aim of mixing plastic with biomass and tyres wastes was to improve the liquid fraction of the products, and to evaluate the H-donor effect of the plastic, as by pyrolysis a liquid medium will be produced which may facilitate mass and heat transfer and consequently further pyrolysis reactions. On the other hand, the presence of plastics might also improve liquids properties and its behavior as a fuel. A mixture of PE, PP and PS, the major plastic components of the Municipal Solid Wastes (MSW) was used in the present study. Pine was the biomass species

selected for this work, because it is the most abundant variety in Portuguese forest. Scrap tyres without any metallic components were also pyrolyzed. Mixtures with these three wastes in different compositions were pyrolyzed to identify and to take profit of any synergetic effects.

2 Materials and methods

2.1 Raw materials

In this work were used recycled wastes of polyethylene, polystyrene and polypropylene previously pelletized to particles with 5 mm of diameter. The biomass used was pine (*pinus pinaster*) in the form of shreds derived from forestry residues with about 2 cm of length and 2 mm of diameter, and the tyres were filaments of the same dimension provided by a scrap tyres recycling plant.

2.2 Experimental

All pyrolysis experiments were conducted in a 1 liter stainless Hastelloy C276 alloy autoclave (by Parr Instruments). Plastics content in the waste mixture was varied from 20 to 80% (w/w) (the difference to 100% in each run was composed by equal parts of pine and tyres). It was kept a constant plastic relative composition of 56% PE, 27% PP and 17% PS, simulating their distribution in the plastics fraction of Portuguese MSW. All tests were carried out with an initial nitrogen pressure of 0.41 MPa. The following range of experimental conditions was used: pyrolysis temperature - 350 to 450ºC and reaction time - 5 to 30 minutes.

Typical curves of temperature and pressure evolution obtained with the apparatus used, showed that the heating of the mixture is a slow process, as the heat transfer from the furnace to the autoclave interior is not readily done. Average low heating rates of 5.5ºC/min were obtained. As waste mixture heating is a slow process for the equipment used, the residence time of the feedstock inside the autoclave from the start of the heating until the end of the cooling till room temperature is much longer than the reaction time, which is referred as the time at which the waste mixture is maintained at the desired pyrolysis temperature.

The gaseous products fraction was analyzed on a Gas Chromatograph (GC) to identify and quantify the major gas components produced with the several pyrolysis reaction conditions. The liquid fraction was distilled according to ASTM D86 [20] to yield three fractions: the lighter hydrocarbons distilled below 150ºC, the second distillate fraction with heavier hydrocarbons (150ºC<bp<270ºC) and the residue (third distillate, bp>270ºC). The first two distillates were analyzed by GC and GC/MS. The distillation curve of the liquid fraction was also compared to the ones of gasoline and diesel. The remaining solid fraction was weighted and extracted with dichloromethane (DCM) and tetrahydrofuran (THF) in a soxhlet extractor (by ASTM D5369-93(2003)) to recover the liquids adsorbed in the solid. The dried solid product was weighted to give the effective pyrolysis yield of solids. The extracted liquids were also subsequently analyzed by GC and GC/MS.

3 Results and discussion

The effect of different experimental parameters on products yields and composition was studied: waste blend composition, reaction time and temperature and initial nitrogen pressure. The value selected for each experimental condition, after the study of its influence

on products yields and composition, was used for the study of the effect of the next parameter. Only the more significant effects will be discussed in this paper.

3.1 Effect of waste blends composition

Four different percentages of the plastics blend on the waste mixture were tested: 20, 40, 60 and 80%. Each of these wastes was subjected to a temperature of 420ºC during 15 minutes. Figure 1 shows the effect of this experimental parameter on products yields. The main fraction obtained was liquids, whose yields changed between 33%, when only pine was pyrolyzed, and 92% when only the plastic mixture was processed. Figure 1 shows that the plastic content of the initial mixture had a marked influence on product yields, increasing the liquid production and decreasing the solid and gas yields.

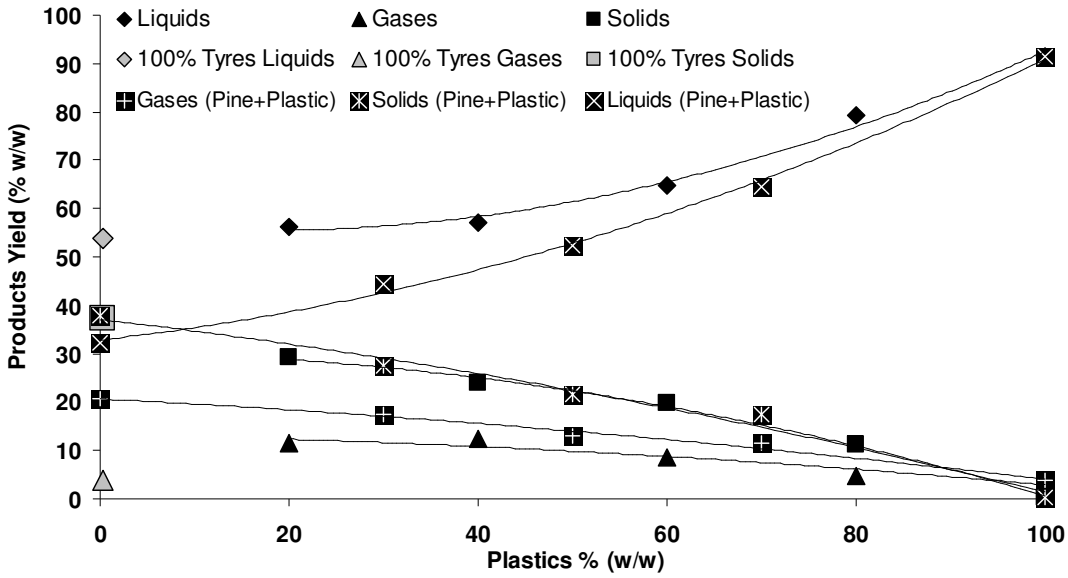

Figure 1: *Influence of the plastic content of the initial mixture on products yields at 420ºC and initial pressure of 0.41MPa, using 15 minutes of reaction time. Solid lines represent the results of this work. Dashed lines refer to pyrolysis of pine and plastic wastes blends [Paradela et al (2009)].*

Comparing these results with those obtained in a previous work when only pine and plastics were pyrolysed [Paradela *et al* (2009)], also showed in Figure 1, it can be observed that the addition of tyres to the mixture seemed to have increased the liquids yield and decreased the gas formation. The solid fraction yields were similar for the two types of mixtures, when plastics content in the mixture were higher than about 40%.

Regarding the composition of the gas fraction the increase of the plastic content of the mixture decreased the percentage of CO2 on the produced gases, while accordingly increased their alkane content. However, methane did not seem to follow this trend, probably because it was also formed in considerable amount, when only pine or tyres were pyrolyzed. The release of CO2 was higher when higher amounts of pine wastes were used in the waste blends, being especially notorious when only pine wastes were pyrolyzed, probably due to the oxygen content of pine. It was also observed that hydrocarbons concentrations decreased with the rise of the number of carbon atoms, being methane content the highest for all the wastes blends studied.

The runs with only pine, only tyres and with 20 and 40% plastics did not yield enough liquids to obtain distillation curves, as most of the liquids produced were impregnated within the solids and had to be extracted with solvents, as mentioned before. Pyrolysis distillations curves of liquids, obtained for the other wastes blends tested, always draw between those of typical gasolines and gas oils, what suggests that liquids chemical composition may be similar to those of gasolines and gas oils. However, while for gasolines and gas oils most of the liquids are distilled, for pyrolysis liquids, distillation had to be usually stopped at temperatures around 270ºC, to prevent the formation of black fumes and the consequent degradation of the liquid. Generally, this happens when 70 to 80% of the initial liquid is distillated, though some variations in these values may be observed, according to liquids composition, which depend on pyrolysis experimental conditions and waste composition.

In the overall liquids production the main compounds were grouped in three major classes: aromatic compounds, alkanes and alkenes. Many compounds were identified in each of these groups, most of them formed in very small amounts. The aromatic compounds formed in higher concentrations, from 8 to 15% (w/w) were toluene, ethylbenzene and sometimes xylenes and other substituted benzenes. Linear alkanes ranging from C5 to C24, and their corresponding 1-alkenes were also identified. It was observed an increase of alkanes and alkenes production and a decrease of aromatic compounds, when higher contents of plastics were used. In the run with only 20% of plastics, the major class of liquid compounds produced was aromatics, which may therefore, be originated from the decomposition of the pine or the tyres.

3.2 Effect of reaction time

Another parameter that was studied was the reaction time. Five different reaction times were tested: 5, 10, 15, 20 and 30 minutes, for a fixed waste mixture composition: 10% Pine, 10% Tyres, 45% PE, 14% PS and 21% PP. The reaction temperature was 420ºC and the initial pressure was 0.41MPa. No significant changes were detected in products yields when reaction time increased from 5 to 30 minutes.

Regarding the gas fraction, the increase of reaction time seemed to increase the alkanes content of the gas, while decreasing the production of CO2 and CO. These experimental results seem to indicate that longer reaction times favored the recombination of smaller radicals to give compounds with higher molecular weight. However, this hypothesis needs to be confirmed by kinetic studies.

For the shortest reaction time tested it was possible to distill only 45% of the liquid obtained by pyrolysis. When longer reaction times were used, pyrolysis liquids composition allowed theirs distillation till higher percentages of liquids and for the longest reaction time, 30 minutes, it was possible to distill around 80% of the initial liquid, before it started to decompose, probably because lighter compounds were produced. With the increase of reaction time, the residual fraction decreased, with a corresponding increase in the first and second distillates. This seems to indicate that lighter compounds were formed by further decomposition of the chains, when longer reaction times were used. Though no significant changes were observed in products yields distribution, these results suggest that longer reactions times favored the formation of lighter compounds.

The alkane content of the liquid fraction increased with the reaction time, with a corresponding decrease in the aromatic compounds content.

3.3 Effect of reaction temperature

The effect of reaction temperature was also studied, by testing five different reaction temperatures: 350, 380, 400, 420 and 450ºC. A fixed waste mixture composition: 10% Pine, 10% Tyres, 45% PE, 14% PS and 21% PP and 20 minutes of reaction time were used for these runs. The increase of the temperature led to a rise of gas and solids production. The same trend was observed in a previous work when a pine and plastics mixture with respectively 30 and 70% was pyrolysed at similar experimental conditions [Paradela *et al* (2009)]. These results seem to indicate that longer reaction times favored the cracking of liquid molecules into smaller ones, which are gaseous at normal temperature and pressure conditions. On the other hand, the recombination of liquid fractions into heavier molecules, which are solid at normal conditions, might also have been favored.

The increase of the reaction temperature favored the production of gaseous alkanes, while reducing the contents of CO and CO2 in the produced gases. This same trend was observed in a previous work when plastics blended with 30% (w/w) of pine wastes was pyrolysed [Paradela *et al* (2009)]. These results also seem to indicate that the rise of reaction time favored the recombination of very small radicals into small gaseous molecules. However, for all the tested temperatures the formation of lighter gaseous hydrocarbons was favored, being methane the compound that presented the highest concentrations for all the tested temperatures. On the other hand, the rise of pyrolysis temperature might also have favored the cracking of liquid molecules into gaseous hydrocarbons.

Again, when using reaction temperatures of 350ºC and 380ºC not enough liquids were obtained to perform their distillation, as most of the liquids produced were impregnated within the solids and had to be extracted with solvents as mentioned before. The use of reaction temperatures higher than 380ºC allowed the production of liquids in enough amounts to be distilled. In fact, at 400ºC only 55% of the pyrolysed liquid was distillated, while at 450ºC it was possible to distillate around 80% before liquid decomposition.

The increase of the reaction temperature seemed to favor the formation of alkanes while decreasing the relative production of aromatic compounds. The alkenes production rose from about 8%, when 350ºC was applied, to a constant value of about 15% when higher temperatures were used.

3.4 Effect of initial pressure of nitrogen

The effect of the initial nitrogen pressure was also studied, by testing five different pressures: 0.2, 0.4, 0.6, 0.8 and 1 MPa. A fixed waste mixture composition: 10% Pine, 10% Tyres, 45% PE, 14% PS and 21% PP, 20 minutes of reaction time and 420ºC of reaction temperature were used for these runs. However, this experimental parameter did not show any appreciable effect in the products distribution and composition.

4 Conclusions

Plastics content in the waste mixture was the experimental parameter that most influenced the pyrolysis of mixtures with pine, plastics and tyres wastes. The rise of plastics content in the blend increased liquids yield (from 33% to 92% w/w) and favored the formation of lighter compounds (less distillation residue). The conversion of aromatic compounds into alkanes and alkenes was also favored by the rise of plastic wastes in the blends, decreasing aromatic compounds contents from 52% to 28% w/w. It was also observed a decrease of CO2

production in the gaseous phase (from 67% to 2% v/v), while the release of hydrocarbons increased, thus leading to a gas with higher energetic content.

Although the rise of reaction time did not affect significantly products distribution, it increased the release of gaseous hydrocarbons (from 64% to 78% v/v) and lowered CO2 and CO contents in the gas fraction (from 29% to 17% v/v). The increase of reaction time also decreased the formation of heavier liquids compounds (less distillation residue), while increased the relative alkanes content of the liquids (48% to 60% w/w).

Pyrolysis reaction temperature favored gas production with higher alkanes content (from 39% to 70% w/w) and although the yields of liquids decreased (82% to 74% w/w) the formation of lighter compounds was favored by the rise of reaction temperature (less distillation residue), together with the formation of both alkane and alkenes, at the expenses of the aromatic compounds (rise from 47% to 70% w/w).

The initial pressure of nitrogen did not seem to produce a significant effect in any of the studied characteristics of pyrolysis products.

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